Miscellaneous Exercise Question Bank

1.(A) $\mathrm{pH} = \mathrm{pK_{in}} + \log\dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]}$, where $\mathrm{pK_{in}} = 6$

For acid colour to predominates $\dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]} \le \dfrac{1}{10}$

$\therefore \quad \mathrm{pH} < 6 - 1$ i.e 5.0

for base colour to predominate $\dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]} \ge 5$

$\therefore \quad \mathrm{pH} \ge 6 + \log 5 \quad \Rightarrow \quad \mathrm{pH} \ge 6.7$

2.(C) "Complete dissociation" implies that interionic attraction has completely ceased to exist. This condition in the case of a solution of strong electrolyte is achieved only at infinite dilution when concentration of solution tends to zero.

3.(D) Solution of weak acid being concentrated, we can use the approximate

$\alpha = \sqrt{\dfrac{\mathrm{Ka}}{\mathrm{C}}}$ i.e. $\alpha \propto \sqrt{\dfrac{1}{\mathrm{C}}}$

Thus, decreasing the conc. to one fourth, α will be doubled. Doubling of α means doubling of percentage ionisation. Hence % ionization will be 2x.

$[\mathrm{H}^+] = \sqrt{\mathrm{Ka}\cdot\mathrm{C}}$ i.e. $[\mathrm{H}^+] \propto \sqrt{\mathrm{C}}$

If the conc. is decreased to one fourth of its original value H^+ ion conc. will be halved. Thus, after dilution $[\mathrm{H}^+] = 0..5\times10^{-3}\mathrm{M}$

$\therefore \quad \mathrm{pH} = 3.3$

4.(C) Buffer capacity $= \dfrac{\text{No. of moles of acid added per litre of buffer}}{\text{change in pH}} = \dfrac{0.006}{0.03} = 0.2$

5.(A) $[\mathrm{Ca}^{2+}][\mathrm{SO}_4^{2-}] = 2.4\times10^{-5}$

$[\mathrm{Ca}^{2+}] = \dfrac{2.4\times10^{-5}}{4.8\times10^{-3}} = 5\times10^{-3}\mathrm{M}$

1 L solution contains 5×10^{-3} mole of Ca^{2+} ions

1000 L solution will contain 5 mole i.e. 200 g Ca^{2+} ions

Taking density of aqueous solution to be unity

1000 kg i.e. 10^6 g solution contains 200g Ca^{2+} ions

Conc. of Ca^{2+} ion = 200 ppm

6.(D) Water remains feebly ionised into H^+ and OH^- ions. H^+ ion does not exist independently but as $\mathrm{H_3O}^+$ as shown below:

$\mathrm{H_2O} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O}^+ + \mathrm{OH}^-$

7.(B) $\mathrm{M(OH)_2}$ will precipitate when $[\mathrm{M}^{2+}][\mathrm{OH}^-]^2 > 4.0\times10^{-10}$

$[\mathrm{OH}^-] > 2.0\times10^{-5}$ molar $\qquad (\because [\mathrm{M}^{2+}] = 1)$

$\mathrm{X(OH)_3}$ will precipitate when

$[X^{3+}][OH^-]^3 > 2.7 \times 10^{-14}$

$\therefore \quad [OH^-] > 3 \times 10^{-5}$ molar $\quad (\because [H^{3+}] = 1)$

Thus $M(OH)_2$ requires less concentration of OH^- ion for precipitation. Hence $M(OH)_2$ will precipitate first.

8.(D) At the point of half neutralization the mixture will be an acid buffer with $\dfrac{[\text{salt}]}{[\text{acid}]} = 1$

$pH = pK_a + \log 1$

$pK_a = 5.7$

$K_a = 2.0 \times 10^{-6}$

9.(A) $[OH^-] = 2 \times 10^{-7}$

$pOH = 14 - pH$ or $-\log[OH^-]$

10.(B) $AgCl \rightleftharpoons Ag^+ + Cl^-$

In $CaCl_2$

$$\begin{array}{lcccc} CaCl_2 & \rightleftharpoons & Ca^{2+} & + & 2Cl^- \\ 0.01 & & 0.01 & & 2 \times 0.01 \end{array}$$

In NaCl

$$\begin{array}{lcccc} NaCl & \rightleftharpoons & Na^+ & + & Cl^- \\ 0.01 & & 0.01 & & 0.01 \end{array}$$

In $AgNO_3$

$$\begin{array}{lcccc} AgNO_3 & \rightleftharpoons & Ag^+ & + & Cl^- \\ 0.05 & & 0.05 & & 0.05 \end{array}$$

Common ion effect is maximum in $AgNO_3$. So, $S_1 > S_3 > S_2 > S_4$

11.(D) Since $pH = 12 \quad \therefore \quad pOH = 14 - 12 = 2$

$\therefore \quad [OH^-] = 10^{-2} M$

We know $Ba(OH)_2 \rightleftharpoons Ba^{++} + 2OH^-$

$\therefore \quad [Ba^{++}] = \dfrac{10^{-2}}{2} M$

$\therefore \quad K_{sp} = [Ba^{++}][OH^-]^2 = \left(\dfrac{10^{-2}}{2}\right) \times \left(10^{-2}\right)^2 = 5 \times 10^{-7} M^3$

12.(B) $Zn^{++} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$

$$\therefore \quad K_h = \frac{\left[Zn(OH)_2\right]\left[H^+\right]^2}{\left[Zn^{++}\right]} \qquad \ldots (1)$$

$Zn(OH)_2 \rightleftharpoons Zn^{++} + 2OH^-$

$$\therefore \quad K_b = \frac{\left[Zn^{++}\right]\left[OH^-\right]^2}{\left[Zn\left(OH\right)_2\right]}, \; K_w = [H^+][OH^-]$$

$$\therefore \quad \frac{K_w^2}{K_b} = K_h$$

13.(A) $K_a = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$

14.(A) $C_6H_5COOH \; + \; NaOH \rightleftharpoons C_6H_5COONa \; + \; H_2O$

After neutralization 0.5 0.5

It is a buffer solution of weak acid and its salt

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$pK_a = 4.2$

$K_a = 6.31 \times 10^{-5}$

15.(A) Old pH = 7

New $[OH^-] = 10^{-2} \times \frac{1}{10} = 10^{-3}$

New $pH = 11$

Change is pH = 4

16.(A) NH_4^+ being a conjugate acid of a weak base NH_4OH will be a strong acid, and thus it would get hydrolysed to give free H^+ ion in solution.

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

Solution of all the other salts will be either alkaline or almost neutral.

17.(B) $CH_3{}^+$ is lewis acid because of vacant orbital.

18.(D) $A_2X_5 \rightleftharpoons 2A^{+5} + 5X^{-2}$

$K_s = [A^{+5}]^2[X^{-2}]^5 = \left(2x\right)^2 \times \left(5x\right)^5 = 4x^2 \times 3125x^5 = 12500\,x^7 = 1.25 \times 10^4 x^7$

19.(D) $CH_3COOAg_{(g)} \rightleftharpoons CH_3COO^-_{(aq)} + Ag^+_{(aq)}$

In acidic/basic medium CH_3COO^- or Ag^+ would react with H^+ or OH^- respectively to increase solubility.

20.(B) K_h for anilinium ion $= 2.4 \times 10^{-5} M$

$$K_h = \frac{K_w}{K_b}$$

$$K_b = \frac{10^{-14}}{2.4 \times 10^{-5}} = 4.1 \times 10^{-10}$$

21.(D) In NH_3 medium acetic acid will be neutralized to form CH_3COONH_4 which being a salt will remain completely ionized. On the other hand CH_3COOH in aqueous solution will be only partially dissociated. Thus, acetic acid will show more conduction in NH_3 than in water

22.(A) Equilibrium constant of the reaction

$A^- + H_2O \rightleftharpoons HA + OH^-$ is really the hydrolysis constant of (K_h) of A^- given as

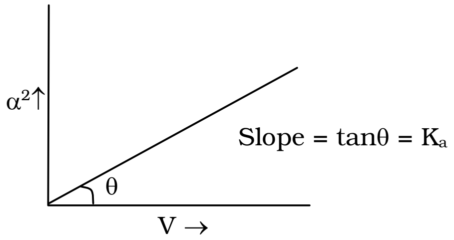
$$K_h = \frac{K_w}{K_a}$$

$$K_a = \frac{K_w}{K_h} = 10^{-8}$$

23.(A) $\alpha = \sqrt{\frac{Ka}{C}}$

$\alpha \propto \sqrt{V}$ or $\alpha^2 \alpha V$

Which an equation of a straight line passing through the origin



24.(B) $[H^+] = [0.5 \times 10^{-3} + 0.5 \times 10^{-4}]$

pH = 3.26

25.(C)

26.(B) $pK_w = 12.26$

$\therefore$ Condition of neutrality pH = 6.13

Thus, pH = 6.2 > 6.13

Means alkaline

27.(B) $HA \rightleftharpoons H^+ + A^-$

$HB \rightleftharpoons H^+ + B^-$

for HA

$K_{a_1} = \alpha^2 C$

$$\alpha_1 = \sqrt{\frac{K_{a_1}}{C}} = \sqrt{\frac{4 \times 10^{-10}}{C}}$$

$\alpha_1 = 2 \times 10^{-5}$ for $C = 1M$

Similarly $[H^+] = C\alpha = 2 \times 10^{-5} \Rightarrow$ pH = 4.7

for HB, $\alpha_2^2 = \sqrt{\frac{K_{a_2}}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{C}} = 1M$

$\alpha_2 = 4.2 \times 10^{-3} \Rightarrow [H^+] = C\alpha = 4.2 \times 10^{-3} \Rightarrow pH = -\log(4.2 \times 10^{-3}) = 2.37$

28.(A) At 25°C, $K_w = 10^{-14}$. So at temperature below 25°C $K_w < 10^{-14}$

$\therefore$ pH > 7 (for neutral solution or pure water)

29.(B) Buffer capacity

$$= \frac{\text{Number of moles of base added / litre of buffer}}{\text{Change in pH}} = \frac{0.01}{(6.832-6.745)} = \frac{0.01}{0.087} = 0.11$$

30.(B) Al^{3+} having high charge density will associate strongly with water through its fractional negatively charged oxygen pole and in such interaction there will be hydrolysis to some extent:

$$Al^{3+} + H_2O \rightleftharpoons [Al(OH)]^{2+} + H^+$$

The product cation may hydrolyse further

31.(B) AgBr forms soluble complex with NH_4OH i.e. $[Ag(NH_3)_2]Br$.

32.(A) When NH_4OH is half neutralized

$[NH_4OH] = [NH_4Cl]$

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{Base}]} = pK_b = 4.75$$

$\therefore \quad pH = 14 - 4.75 = 9.25$

33.(D) $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$\Rightarrow \quad 1.2 \times 10^{-11} = 0.1 \times [OH^-]^2 \quad \Rightarrow \quad [OH^-] = 1.2 \times 10^{-10}$

$\therefore \quad [OH^-] = 1.1 \times 10^{-5}$

$$\therefore \quad [H^+] = \frac{10^{-14}}{1.1 \times 10^{-5}} = 9.09 \times 10^{-9} M$$

$\therefore \quad pH = -\log(9.09 \times 10^{-10}) = 10 - 0.9586 = 9.04$

34.(A) As [salt] = [acid], $pH = pK_a = 9.30$

35.(C) Blood buffers do not allow a change in pH it contains serum protein which act as buffer.

36.(D) $K_{sp} = [A^{3+}]^2[X^{2-}]^3 = (2s)^2(3s)^3 = 108s^5$

37.(C) For hydrolysis of $B^+ + K_h = \dfrac{K_w}{K_b} = \dfrac{10^{-14}}{10^{-6}} = 10^{-8}$

38.(C) $CN^- + H_2O \longrightarrow HCN + OH^-$

$pK_b = 4.7$

$\therefore \quad pK_a = 9.3$

$$[OH^-] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h C} = \sqrt{\frac{K_w C}{K_a}} = \sqrt{\frac{10^{-14} \times 0.5}{10^{-9.3}}}$$

$\therefore \quad [OH^-] = \sqrt{10^{4.7} \times 0.5}$

$\therefore \quad pOH = 11.5$

39.(C) $[H^+] = C\alpha = 0.1 \times 0.013 = 1.3 \times 10^{-3}$

$pH = -\log(1.3 \times 10^{-3}) = 3 - 0.11 = 2.89$

40.(A) $NH_4OH + HCl$ forms NH_4Cl which gives acidic solution with $pH < 7$

41.(A) $BaCl_2$ is the limiting reagent

42.(C) $pH = pK_a + \log\dfrac{[salt]}{[acid]}$

$$\Rightarrow \quad 9 = -\log(5\times10^{-5}) + \log\frac{[salt]}{[acid]} \quad \therefore \quad \frac{[salt]}{[acid]} = 0.5$$

Let volume of KCN to be added is = v

Total volume of HCN + KCN = (10 + v)

$$[KCN] = \frac{5V}{(10+v)}, \ [HCN] = \frac{10+2}{(10+v)}$$

$$\therefore \quad \frac{[salt]}{[acid]} = \frac{5v/(10+v)}{20/(10+v)} = 0.5$$

$$\therefore \quad \frac{v}{4} = 0.5 \quad \therefore \quad v = 2\,cc$$

43.(D) Mixture of sodium acetate and acetic acid is a buffer of pH value equal to pK_a so its buffer capacity is very high and hence its pH will not change significantly while CH_3COONH_4 is a salt of weak acid CH_3COOH and weak base NH_4OH whose magnitude of K_a and K_b are equal. So its pH does not depend upon concentration. Further more, NaH_2PO_4 is, in fact, a single solute buffer.

44.(B) $M(OH)_x$ will ionize in the way

$$M(OH)_x \rightleftharpoons M^{x+} + x\,OH^-$$

$$\qquad\qquad 10^{-4} \qquad x\times10^{-4}$$

$$\therefore \quad K_{sp} = [M^{x+}][OH^-]^x$$

$$\therefore \quad (10^{-4})(x\times10^{-4})^x = 4\times10^{-12}$$

By inspection we get this relation will hold good when x = 2

45.(C) $pH = pK_a + \log\dfrac{[Salt]}{[Acid]}$

$$\therefore \quad 4.5 = 4.2 + \log\frac{[Salt]}{[Acid]} = \log\frac{[Salt]}{[Acid]} = 0.3 \qquad (\text{since } \log 2 = 0.3)$$

$$\therefore \quad \frac{[Salt]}{[Acid]} = 2$$

Let V ml 1M C_6H_5 COOH solution and (300 – V) 1M C_6H_5COONa solution be mixed together

$$[Acid] = \frac{V\times1}{1000}\times\frac{1000}{300}; \qquad [Salt] = \frac{(300-V)}{1000}\times\frac{1000}{300}$$

$$[Acid] = \frac{V}{300}; \qquad [Salt] = \frac{300-V}{300}$$

$$\therefore \quad \frac{300-V/300}{V/300} = 2 = 300 - V = 2V \quad \therefore \quad V = 100\,ml$$

46.(D) Buffer capacity $= \dfrac{\text{moles of acid or base added per litre}}{\text{change in pH}}$

$$\text{Buffer capacity } = \frac{\frac{0.2 \times 10}{1000} \times \frac{1000}{250}}{6.34 - 6.32} = 0.4$$

47.(A) $B(OH)_2 + 2H^+ \rightleftharpoons B^{2+} + 2H_2O$

$$K = \frac{1}{K_h}$$

K_h for hydrolysis of B^{2+}

$$= \frac{[B(OH)_2][H^+]^2}{[B^{2+}][OH^-]^2} \times [OH^-]^2 = \frac{K_w^2}{K_b}$$

$$K_h = \frac{10^{-28}}{10^{-8}} = 10^{-20} \quad \Rightarrow \quad \frac{1}{K_h} = 10^{20}$$

48.(A) $pK_{in} = -\log K_{ln} = 10 - \log 4 = 9.4$

Thus, it is the equivalent point. pH colour change starts from $(pK_{ln} - 1)$ and completes at $(pK_{ln} + 1)$.

49.(A) $[H^+] = 10^{-3}$

$[H^+] = \sqrt{KaC}$

$(10^{-3})^2 = Ka \times 0.1$

$Ka = 10^{-5}$

$HA + NaOH \rightleftharpoons NaA + H_2O \;\; K_N$

$$K_N = \frac{Ka}{Kw} = \frac{10^{-5}}{10^{-14}} = 10^9$$

50.(A)

	ACl_2	+ $2\,NaOH$	$\rightleftharpoons$ $A(OH)_2$	+ $2\,NaCl$
Initially	10	20	0	0
After reaction	0	0	10	20

$[OH^-]^2[A^+]^2 = K_{sp}$

$4s^3 = K_{sp}$

$$s = \sqrt[3]{\frac{1.2 \times 10^{-11}}{4}} = 1.4 \times 10^{-4}$$

$[OH^-] = 2.8 \times 10^{-4}$

51.(A) Eq. of acid = Eq. of base = 20 × 0.1 = 2

HA	+ BOH	$\longrightarrow$ BA	+ H_2O
2	1.2	0	0
0.8	0	1.2	1.2

$$pH = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$5 = -\log K + \log \frac{[1.2]}{[0.8]}$$

$$\Rightarrow \quad K_a = \text{antilog } 4.8 = 1.5 \times 10^{-5}$$

52.(A) $pH = -\log 1.8 \times 10^{-5} + \log \frac{0.164/84}{0.001} = 4.74 + 0.3010 = 5.0457 = -\log[H^+]$

$$\Rightarrow \quad [H^+] = 9 \times 10^{-6}$$

53.(B) For acid indicator HIn,

$$HIn \rightleftharpoons H^+ + In^-$$

Colour (A)   Colour (B)

$K_{In} = \frac{\left[H^+\right]\left[In^-\right]}{\left[HIn\right]}$ when $[In^-] = [HIn]$ indicator changes colour.

$$\therefore \quad K_{HIn} = [H^+] = 1 \times 10^{-5}$$

$$\therefore \quad pH = 5$$

54.(C) $K_a \times K_w = K_\omega \quad \Rightarrow \quad K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.75 \times 10^{-4}$

55.(A) Meq.of KOH = 50 × 0.2 = 10

Meq.of HCOOH = 40 × 0.2 = 20

$\therefore$ Meq.of HCOOH left = 10 Meq. of HCOOK formed = 10

$$\therefore \quad pH = pK_a + \log \frac{\left[\text{salt}\right]}{\left[\text{acid}\right]}$$

$$\Rightarrow \quad pH = -\log K_a + \log \frac{10}{10} \quad \Rightarrow \quad pH = -\log K_a + \log \frac{10}{10}$$

$$\Rightarrow \quad pH = -\log\left(1.8 \times 10^{-4}\right) = 3.75$$

56.(A) $K = C\alpha^2 = 55.5 \times (1.8 \times 10^{-9})^2 = 1.8 \times 10^{-16}$

57.(A) $C_6H_5COOH + NaOH \rightleftharpoons C_6H_5COONa + H_2O$

Final 0.5 0.5

It is a buffer solution of weak acid and its salt.

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pK_a = 4.2$$

$$K_a = 6.31 \times 10^{-5}$$

58.(A) $pH_{old} = 7$

$$[OH^-]_{new} = 10^{-2} \times \frac{1}{10} = 10^{-3}$$

$$\therefore \quad [H^+]_{new} = 10^{-11}$$

$pH_{new} = 11$, Change in pH = 4

59.(BC) For neutral solution, $[H^+]$ must be always equal to $[OH^-]$

60.(B) For colour characteristic of H indicator

$$pH = pK_{in} - \log\frac{[HIn]}{[In^-]}$$

Indicator's colour range

$$pH = pK_{in} \pm 1$$

61.(A) First dissociation

$$X(OH)_3 \longrightarrow X(OH)_2^+ + OH^-$$

Second dissociation:

$$X(OH)_2^+ \longrightarrow X(OH)^{2+} + OH^-$$

Total $[OH^-] = 4\times10^{-3} + 2\times10^{-3} = 6\times10^{-3}$

pOH = 3 – log 6 $\simeq$ 2.22

$\therefore$ pH = 11.78

62.(AC) Apply $N_1V_1 = N_2V_2$ in each case.

(A) $[H^+] = \dfrac{100\times0.1}{150} = 0.67$

(B) $\dfrac{50\times0.2}{100} = 0.1\text{ M}$

(C) $\dfrac{50\times0.2}{150} = 0.67\text{ M}$

(D) $\dfrac{50\times0.1}{100} = 0.05\text{ M}$

63.(BC) Only (B) and (C) are the correct answers.

64.(ABC)

Buffer solution can be prepared from (A), (B) and (C) [In case of (B), sodium acetate reacts with HCl to form $CH_3COOH + NaCl$].

65.(ABC)

(A), (B), (C) are the correct answers but (D) is wrong.

66.(BCD)

(B) and (D) function as buffer. (C) is not because both are acidic salts but one of them should be a normal salt.

67.(C) Let the volume of KCN = x ml, then for acidic buffer

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$\Rightarrow\quad 9 = 10 - \log 5 + \log\frac{5x}{20} \quad\Rightarrow\quad 9 = 10 - \log 5 - \log\frac{4}{x}$$

$$\Rightarrow\quad 9 = 10 - \log\frac{20}{x} \quad\Rightarrow\quad \log\frac{20}{x} = 1 \quad\Rightarrow\quad \frac{20}{x} = 10$$

$$\Rightarrow\quad x = 2\text{ ml}$$

68.(B) $pH = \dfrac{pK_{a_1} + pK_{a_2}}{2}$

69.(A) $[H^+] = 10^{-13}$ i.e. 10^{-13} mol in 1 L

No. of H^+ in 1000 ml $= 6.02\times10^{23}\times10^{-13}$

$= 6.02\times10^{10}$

No. of H^+ in 1 ml $= 6.02\times10^{7}$

70.(A)

71.(D) $Fe^{3+}(aq.) + H_2O(l) \rightleftharpoons Fe(OH)^{2+}(aq.) + H_3O^+(aq.)$

$$K_a = \frac{[Fe(OH)^{2+}][H_3O^+]}{[Fe^{3+}]}$$

$$\Rightarrow \ 6.5 \times 10^{-3} = \frac{0.20}{0.80} \times [H_3O^+]$$

$$\Rightarrow \ [H_3O^+] = 2.6 \times 10^{-2}; \quad pH = 1.59$$

72.(B) 10^6 g water is associated with 746 g i.e. $\frac{746}{373} = 2$ mole of $CsBr_3$

$\therefore$ 10^3g 1 L ($\because$ d = 1) is dissociated with 2×10^{-3} mole of $CsBr_3$

Thus, solubility of $CsBr_3 = 2 \times 10^{-3} M$

$$CsBr_3(s) \rightleftharpoons Cs^+(s) + Br_3^-(s)$$

$$K_{sp} = S^2 = 4 \times 10^{-6} M^2$$

73.(B) After mixing $[Ag^+] = 0.2\,M; [NH_3] = 1\,M$

Due to very high value of K_f; Ag^+ mainly converted into complex

	$Ag^+(aq.)$	$+ 2NH_3(aq.) \rightleftharpoons$	$Ag(NH_3)_2^+(aq.)$
Initial concentration	0.2	1	
At equilibrium	x	0.6	$\simeq 0.2$

	$Ag(NH_3)_2^+(aq.) \rightleftharpoons$	$Ag(NH_3)^+(aq.)$	$+ NH_3(aq.)$
At equilibrium	$0.2 - y$ $\simeq 0.2$	y	$0.6 + y$ $\simeq 0.6$

$$\frac{1}{K_{f_2}} = \frac{y \times 0.6}{0.2} \Rightarrow \frac{0.1}{10^4}; y = [Ag(NH_3)^+] \Rightarrow 3.33 \times 10^{-5} M$$

74.(A) $AgCl(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Cl^-(aq.)$

$$K_1 = 1.6 \times 10^{-10} \times 10^7 = 1.6 \times 10^{-3}$$

$$= \frac{[Ag(NH_3)_2^+][CN^-]}{[NH_3]^2}$$

$AgCN(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Cl^-(aq.)$

$$K_2 = 2.5 \times 10^{-16} \times 10^7 = 2.5 \times 10^{-9}$$

$$= \frac{[Ag(NH_3)_2^+][CN^-]}{[NH_3]^2}$$

$$\frac{[Cl^-]}{[CN^-]} = \frac{1.6\times10^{-3}}{2.5\times10^{-9}} = 6.4\times10^{5}$$

$$K_1 = \frac{x^2}{(1-2x)^2} \Rightarrow \frac{x}{1-2x} = 0.04$$

$x = 0.037$

$$\therefore \quad [CN^-] = \frac{0.037}{6.4\times10^{5}} = 5.78\times10^{-8}$$

75.(B) $[Ca(OH)_2] = [Ca\,(OH)_2] = \dfrac{5\times10^{-4}\times1000}{100} = 5\times10^{-3}$ mole L^{-1}

$[OH^-] = 2\times5\times10^{-3} = 10^{-2}$ mole L^{-1}

$$[H^+] = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$pH = -\log 10^{-12} = 12$

76.(C) Moles of $CaCO_3$ in residue $= \dfrac{7\times10^{-3}}{100} = 7\times10^{-5}$

Moles of $CaCO_3$ in 1 litre solution $= 7\times10^{-5}$

$$\begin{array}{lcccc} CaCO_3(s) & \rightleftharpoons & Ca^{2+} & + & CO_3^{2-} \\ & & 7\times10^{-5} & & 7\times10^{-5} \end{array}$$

$K_{sp} = [Ca^{2+}]\times[CO_3^{2-}] = 7\times10^{-5}\times7\times10^{-5} = 4.9\times10^{-9}$

77.(D) $TCl + NaOT \longrightarrow NaCl + T_2O$

Initial 2 3.75

Milli-moles

Milli-moles of remaining NaOT = 1.75

$\therefore \; [OT^-] = \dfrac{1.75}{25} = 7\times10^{-2}$ moles

pOT = 2 – log 7

pT + pOT = 7.62 × 2

$\therefore \; pT = 15.24 - 2 + \log 7$

$= 13.24 + \log 7$

78.(C) HPO_4^{2-} is amphiprotic and it involves pK_{a_2} and pK_{a_3}

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $\qquad K_{a_3}$

$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$ $\qquad \dfrac{1}{K_{a_2}}$

For such cases

$$pH = \frac{pK_{a_2} + pK_{a_3}}{2} = \left(\frac{y+z}{2}\right)$$

79.(B) Precipitation occurs when the ionic product exceeds the K_{sp} value. When equal volumes of two solutions are mixed the concentration of each is reduced to half. Therefore,

In first case,

$$\text{Ionic product, I.P.} = \left(\frac{1}{2}\times 10^{-4}\right)^2\left(\frac{1}{2}\times 10^{-4}\right) = \frac{1}{8}\times 10^{-12} = 1.25\times 10^{-13}$$

As, $\text{I.P.} < K_{sp}$ $\quad\therefore\quad$ No precipitation occurs.

In second case,

$$\text{I.P.} = \left(\frac{1}{2}\times 10^{-2}\right)^2\left(\frac{1}{2}\times 10^{-3}\right) = \frac{1}{8}\times 10^{-7} = 1.25\times 10^{-8}$$

As, $\text{I.P.} > K_{sp}$ $\quad\therefore\quad$ precipitation occurs

In third case,

$$\text{I.P.} = \left(\frac{1}{2}\times 10^{-5}\right)^2\left(\frac{1}{2}\times\ 10^{-3}\right) = \frac{1}{8}\times 10^{-13} = 1.25\times 10^{-14}$$

As, $\text{I.P.} < K_{sp}$ $\quad\therefore\quad$ no precipitation occurs

In fourth case,

$$\text{I.P.} = \left(\frac{1}{2}\times 10^{-4}\right)^2\left(\frac{1}{2}\times\ 10^{-5}\right) = \frac{1}{8}\times 10^{-13} = 1.25\times 10^{-14}$$

As, $\text{I.P.} < K_{sp}$ $\quad\therefore\quad$ no precipitation occurs

80.(A) The reaction is the reverse of the ionization reaction of HA, hence the equilibrium constant is the reciprocal of K_a.

$$K = \frac{[\text{HA}]}{[\text{A}^-]\ [\text{H}^+]} = \frac{1}{K_a} = \frac{1}{1.0\times 10^{-6}} = 1.0\times 10^{6}$$

81.(C) $\text{HCO}_2\text{H} \rightleftharpoons \text{H}^+ + \text{HCO}_2^-$

$0.001 - x \qquad x \qquad x$

α is > 0.1 which means x is not ignorable.

$$\therefore \qquad K_a = 1.8\times 10^{-4} = \frac{x^2}{0.001 - x}$$

Solving by quadratic,

$$x = 3.4\times 10^{-4}$$

check for α

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$\alpha = \sqrt{\frac{1.8\times 10^{-4}}{0.001}} = 0.42$$

$$\therefore \qquad \%\text{ ionization} = \frac{\text{ionized HCO}_2\text{H}}{\text{total HCO}_2\text{H}}\times 100 = \frac{3.4\times 10^{-4}}{0.001}\times 100 = 34\,\%$$

82.(A) $2\text{NH}_3(\ell) \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$

$1 - x \qquad x \qquad x$

(Neglecting x in comparison to 1 since K_{NH_3} is very small).

$$K_{\text{NH}_3} = x^2 = -10^{30}$$

thus, $x = 10^{-15}M = [NH_2^-]$

$$[NH_2^-] = 10^{-15}\text{ moles / lit} = \frac{10^{-15}}{10^6}\text{ moles / mm}^3$$

$$[NH_2^-] = 10^{-21} \times 6 \times 10^{23}\text{ ions / mm}^3 = 600\text{ ions / mm}^3$$

83.(D)
$$\begin{array}{ccccc} C_6H_5NH_3^+CH_3CO_2^- & \rightleftharpoons & C_6H_5NH_3^+ & + & CH_3CO_2^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$K_{eq} = \dfrac{c\alpha^2}{(1-\alpha)}$ assuming α to be small, $(1-\alpha) \approx 1$

$$\therefore \quad \alpha = \sqrt{\frac{K_{eq}}{c}}$$

84.(CD) Let the initial equivalent of BOH are x.

$$\begin{array}{ccccccc} BOH & + & HCl & \longrightarrow & BCl & + & H_2O \\ x & & 3/4x & & 0 & & 0 \\ x - \frac{3}{4}x = \frac{x}{4} & & 0 & & \frac{3}{4}x & & \frac{3}{4}x \end{array}$$

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} = 5 + \log\frac{3x+4}{4+x}$$

$$pH = 14 - 5 - \log 3 = 8.523$$

85.(C) $pH = 7 + 1/2\left(pK_a - pK_b\right) = 7 + 1/2\left(4.8 - 4.78\right) = 7.01$

86.(C) Mixture of CH_3COOH & CH_3COONa is a buffer

87.(C)
$$\begin{array}{lccc} & CH_3COOH(aq) \rightleftharpoons & CH_3COO^-(aq) + & H^+(aq) \\ t = t_{eq} & 0.01 - 10^{-4} & 10^{-4} & 10^{-4} \end{array}$$

Since K is same for both

$$\begin{array}{lccc} & NH_4OH_{(aq)} \rightleftharpoons & NH_{4(aq)}^+ + & OH^-_{(aq)} \\ t = t_{eq} & 0.01 - 10^{-4} & 10^{-4} & 10^{-4} \end{array}$$

$\Rightarrow \quad pOH = 4 \;\Rightarrow\; pH = 10$

88.(C) $\underset{Red}{HA} \rightleftharpoons H^+ + \underset{Blue}{A^-}$

$$pK_a = 5 - \log 3$$
$$= 5 - 0.47 = 4.53$$

For 75% red

$$pH = 4.53 + \log\frac{25}{75}$$
$$= 4.53 - \log\frac{1}{3} = 4.05$$

For 75% blue,

$$pH = 4.53 + \log\frac{75}{5}$$
$$= 4.53 + 0.47 = 5$$

89.(D) (50 ml, 0.2 M) (75 ml, 0.1 M)

	NH_4Cl	+	$NaOH \longrightarrow$	$NH_4OH + NaCl$
	10 mmoles		7.5 mmoles	
At eq.	2.5 mmoles			7.5 mmoles

$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]} = 4.74 + \log\frac{2.5}{7.5} = 4.27$$

$pH = 14 - 4.27 = 9.73$

90.(A) $K_b(X^-) = 10^{-10}$

$\therefore$ K_a for $HX = 10^{-4}$

$pK_a = 4$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$pH = 4$

91.(8.63)

At equivalence point, the equivalents of NaOH added would be equal to the equivalents of CH_3CO_2H and the same equivalents of CH_3CO_2Na is formed. This salt would undergo hydrolysis. As the salt is made up of weak acid and strong base,

$$\therefore \quad [H^+] = \sqrt{\frac{K_wK_a}{c}}$$

First of all we would calculate the concentration of the salt, CH_3COONa. For reaching equivalence point,

$N_1V_1 = N_2V_2$

$\therefore$ $0.1 \times 25 = 0.05 \times V_2$

$V_2 = 50$ ml

$$\text{Therefore } [CH_3COONa] = \frac{0.1 \times 25}{75} = \frac{0.1}{3}$$

$$\therefore \quad [H^+] = \sqrt{\frac{10^{-14} \times 1.8 \times 10^{-5}}{0.1/3}} = 2.32 \times 10^{-9}$$

$$pH = -\log 2.32 \times 10^{-9} = 8.63$$

92.(28.72 mL)

Let the molarity of HA is M_2 and the molarity and volume of weak base (BOH) are M_1 and V_1 respectively. In first case,

	BOH	+ $HA \longrightarrow$	BA	+ H_2O
mmole before reaction	M_1V_1	$10M_2$	0	0
mmole after reaction	$(M_1V_1 - 10M_2)$	0	$10M_2$	$10M_2$

$$\therefore \quad pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$14 - 10.2 = pK_b + \log\frac{10M_2}{(M_1V_1 - 10M_2)}$$

Dividing numerator and denominator of log term by M_2

$$\therefore \qquad 3.8 = pK_b + \log \frac{\dfrac{10M_2}{M_2}}{\left(\dfrac{M_1V_1}{M_2} - \dfrac{10M_2}{M_2}\right)}$$

$$3.8 = pK_b + \log \frac{10}{V_2 - 10} \qquad \text{....... (i)}$$

where V_2 is the volume of acid required to attain equivalence point (At equivalence point, $M_1V_1 = M_2V_2$)

In second case,

	BOH	+	HA	$\longrightarrow$	BA	+	H_2O
mmole before reaction	M_1V_1		$25M_2$		0		0
mmole after reaction	$(M_1V_1 - 25M_2)$		0		$25M_2$		$25M_2$

$$14 - 9.1 = 4.9 = pK_b + \log \frac{25M_2}{(M_1V_1 - 25M_2)}$$

Dividing numerator and denominator of log term by M_2

$$4.9 = pK_b + \log \frac{25}{V_2 - 25} \qquad \text{....... (ii)}$$

Substracting equation (i) from (ii)

$$4.9 - 3.8 = 1.1 = \log \frac{25}{V_2 - 25} - \log \frac{10}{V_2 - 10}$$

Taking antilog $12.58 = \frac{5V_2 - 50}{2V_2 - 50}$

$\therefore \qquad V_2 = 28.72\,\text{mL}$

93. We shall assume that the Ag^+ is completely converted into the higher complex $Ag(NH_3)_2^+$, by the excess of NH_3. Therefore,

$$[Ag(NH_3)_2^+] = 1.0 \times 10^{-3} M$$

$$[NH_3] = 2 \times 10^{-1} - 2.0 \times 10^{-3} = 2 \times 10^{-1} M$$

From the instability constant, we have

$$\frac{[Ag^+]\ [NH_3]^2}{[Ag(NH_3)_2^+]} = (1.4 \times 10^{-4})(4.3 \times 10^{-4})$$

$$[Ag^+] = (6.02 \times 10^{-8}) \frac{[Ag(NH_3)_2^+]}{[NH_3]^2} = \frac{(6.02 \times 10^{-8})\ (1.0 \times 10^{-3})}{(2 \times 10^{-1})^2} = 1.505 \times 10^{-9} M$$

The concentration of $Ag(NH_3)^+$ may be obtained from either of the stepwise dissociation constants. Thus

$$\frac{[Ag(NH_3)^+]\ [NH_3]}{[Ag(NH_3)_2^+]} = 1.4 \times 10^{-4} M$$

$$[Ag(NH_3)^+] = \frac{(1.4 \times 10^{-4})[Ag(NH_3)_2^+]}{[NH_3]} = \frac{(1.4 \times 10^{-4})\ (1.0 \times 10^{-3})}{0.2} = 0.7 \times 10^{-6} M$$

94.(A) $Ba(OH)_2 \rightleftharpoons \underset{s}{Ba^{2+}_{(aq)}} + \underset{2s}{2OH^-_{(aq)}}$

pH = 12 $\quad\therefore\quad$ $pOH = 2$ or $[OH^-] = 10^{-2}$

$2s = 10^{-2}$ or $s = \frac{1}{2} \times 10^{-2}$

$$K_{sp} = 4s^3 = 4 \times \left(\frac{1}{2} \times 10^{-2}\right)^3 = 4 \times \frac{1}{2} \times 10^{-6} = 5 \times 10^{-7} M$$

95.(C) For just k precipitation of AgCl

$[Ag^+][Cl^-] = 10^{-10}$

$[Ag^+] = \frac{10^{-10}}{0.05} = 2 \times 10^{-9}$

$\therefore \quad [Ag^+][I^-] = 4 \times 10^{-16}$

$[I^-] = \frac{4 \times 10^{-16}}{2 \times 10^{-9}} = 2 \times 10^{-7} M$

96. $Q_{SP} = [Ag^+][I^-] = 0.01 \times 0.015 = 1.5 \times 10^{-4}$

Since $Q_{sp} > K_{sp}$

AgI will precipitate

97.(B) $Ca(OH)_2 \rightleftharpoons \underset{s}{Ca^{2+}(aq)} + \underset{2s}{2\,OH^-(aq)}$

$4s^3 = 5.5 \times 10^{-6}$

$s = 1.1 \times 10^{-2}$

$[OH^-] = 2.2 \times 10^{-2}$

$pOH = 2 - \log 2.2 = 1.66$

$pH = 14 - 1.66 = 12.34$

98.(B) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ $\qquad K_a = 1.8 \times 10^{-5}$

$\alpha = \sqrt{\frac{Ka}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.5}} = 6 \times 10^{-3}$

99.(A) $[H^+] = C\alpha$

$= 0.5 \times 6 \times 10^{-3} = 3 \times 10^{-3}$

$pH = 3 - \log 3 = 2.52$

100.(B) $\underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong acid}}{HCl}$

$HCl \longrightarrow H^+ + Cl^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

In this case, H^+ from CH_3COOH can be ignored (common ion effect)

$[H^+] = \frac{0.1 \times 100}{200} = 0.05\ M = 5 \times 10^{-2} M$

$pH = 2 - \log 5 = 2 - 0.7 = 1.3$